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Nitrogen isotopes in intra-crystal coralline aragonites

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ABSTRACT

To assess the preservation of the nitrogen isotope composition in reef corals, nitrogen isotopes in a well-preserved Pliocene fossil coral (located in the Tartaro formation on Luzon Island, Philippines (14°N, 121°E)) and in a modern coral (Kochi, Japan (32°N, 132°E)) were analysed using stepwise heating methods. The thermal decomposition of aragonite triggered the largest release of nitrogen at 700 °C for the modern coral and 550 °C for the Pliocene coral. The highest rate of nitrogen gas emission occurred at the aragonite collapse temperature, indicating that organic nitrogen was bound within the intra-crystals of coralline aragonites in both corals. After the aragonite collapsed in both corals, the nitrogen isotope ratios increased due to fractionation and then decreased to values similar to those observed in bulk samples of the modern (+10.1‰) and Pliocene (+4.4‰) corals. These results suggested that fresh organic nitrogen was released due to the decomposition of the internal skeletal structure at higher temperatures (900–1000 °C). Nitrogen isotopes in coral skeletons were preserved in intra-crystal aragonite, even in a Pliocene fossil, and stepwise heating methods were shown to be useful for determining the preservation of coralline nitrogen isotopes.

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1. Introduction

The nutrient cycle in surface oceans regulates primary production, which influences the carbon dioxide concentration in the atmosphere. Global warming and cooling have occurred repeatedly over geological time scales and are often accompanied by nutrient concentration changes, especially in the polar and tropical oceans (Sigman and Boyle, 2000). Understanding nutrient circulation changes over geological time scales is useful for predicting future environmental changes. The nitrogen isotope proxy in coral skeletons ($\delta^{15}N_{coral}$) may be applied to fossil corals for the reconstruction of palaeo-nitrogen cycles. Modern and fossil coral skeletons have been used as high-resolution recorders of surface ocean environments at low latitudes (e.g., Gagan et al., 2000; Correge, 2006; Watanabe et al., 2011). The modern $\delta^{15}N_{coral}$ is a record of the high-resolution dynamics of nitrogenous nutrients in surface oceans (Yamazaki et al., 2011a,b). According to the fossil records, corals belonging to the Anthozoa class originated in the Palaeozoic era (Scrutton, 1997), and scleractinian corals appeared in the middle of the Triassic period (~237 Ma) (Stanley and Fautin, 2001). Muscatine et al. (2005) showed that the nitrogen isotope composition in Triassic coral skeletons is similar to that of modern symbiotic coral skeletons. The authors suggested that Triassic corals possessed symbiotic algae and preserved the nitrogen isotope composition in their intra-crystal skeletons. However, few studies have explored the application of nitrogen isotope proxy records in fossil corals over long periods of time because methods that can be used to confirm that organic nitrogen was preserved in intra-crystal coralline aragonites have not yet been developed, even in fossils. In the present study, the preservation of the nitrogen isotope composition in modern and fossil corals was examined using stepwise heating analysis. Stepwise heating methods have been used in the analysis of noble gases and nitrogen in rock samples (e.g., Reynolds et al., 1970; Sano and Pillinger, 1990). This technique has been applied to nitrogen isotopes of modern coral by Uchida et al. (2008) to detect trace nitrogen in coral skeletons. We divided the heating process into seven steps (200 °C to 1000 °C) to determine the aragonite collapse temperature and the nitrogen isotope ratios preserved in extra- and intra-crystalline aragonite. We used well-preserved Pliocene fossil corals (3.5–3.8 Ma) collected from Luzon Island, Philippines, which is located in the western Pacific warm pool. In the middle of the Pliocene epoch, the annual mean temperature was 2–4 °C warmer than that under preindustrial conditions (Haywood and Valdes, 2004; Brierley et al., 2009; Haywood et al., 2009). Pliocene coral specimens may contain nutrient circulation data in tropical warm pools under global-warming-like conditions.

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2. Methods

2.1. Modern coral specimen

To decrypt the $\delta^{15}N_{coral}$ pattern of the Pliocene coral, we compared it with modern $\delta^{15}N_{coral}$ in a living *Porites* coral skeleton from Tatsukushi Bay, Kochi, Japan (32°N, 132°E). We measured modern coral skeletons using the chemical conversion methods described by Yamazaki et al. (2011a) to validate the bulk $\delta^{15}N_{coral}$ values of modern coral skeletons. A rectangular coral skeleton ($10 \times 40 \times 7$ mm) containing 5 annual bands was cut from the coral colony and powdered using an agate mill to obtain a heterogeneous powder. To remove any organic materials attached to the outer crystals, the coral powder was placed in polypropylene tubes, soaked in NaOH (2 N) and placed inside a dry bath (60 °C). Treatment times of 0, 0.5, 1, 2, 3, and 5 h were tailored to capture intra-crystalline nitrogen. During the treatment process, NaOH and coral powder were mixed once every hour using the tube mixer. At each treatment step, the nitrogen isotope content was determined in 5 samples, and those that exhibited a poor recovery rate during the chemical conversion process were excluded from further analysis. The $\delta^{15}N_{coral}$ and total nitrogen content varied widely, especially when the samples were not cleaned (Fig. 1). After 5 h of cleaning, the average $\delta^{15}N_{coral}$ value in the modern coral was $+9.1 \pm 1.5$ (2σ)‰, and the average total nitrogen content was 63 ± 43 (2σ) ppm. The range (2σ) of $\delta^{15}N_{coral}$ and the total nitrogen values were generally in accordance after 1 h and in subsequent steps. The heterogeneity of nitrogen released at every cleaning step was attributed to the spatial distribution of nitrogen components, the seasonal variability of $\delta^{15}N_{coral}$ and of the total nitrogen (Yamazaki et al., 2011b) content and differences in the nitrogen recovery rates throughout the chemical conversion process.

2.2. Fossil coral specimen

Porites specimens were excavated from the Tartaro formation located on Luzon Island, Philippines (14°N, 121°E). A previous study on the nanofossil assemblages showed that the age of the fossils was approximately 3.5–3.8 Ma (Watanabe et al., 2011). The well-preserved fossil coral was selected by conducting a diagenetic alteration test using X-ray radiography, X-ray diffraction analysis, micro-analysis of thin sections via high-energy synchrotron X-ray diffraction, scanning electronic microscopy observations, and optical microscopy observations (Watanabe et al., 2011). Oxygen isotopes ($\delta^{18}O$) were preserved without diagenetic alteration from aragonite to calcite. We used a fossil coral without diagenetic alterations to determine the intra-crystalline nitrogen content using stepwise heating methods.

2.3. Stepwise heating methods

Cubic samples of modern and fossil corals were obtained from each colony, cleaned using milli-Q water in an ultrasonic bath for 20 min and dried in an oven (40 °C) for 2 days. Rectangular samples $5 \times 3 \times 3$ mm in size, which captured approximately 1 year of calcification, were used to adjust the estimated quantity of nitrogen to the mass spectrometer. The sample weights of modern and fossil corals were 17.89 and 17.93 mg, respectively. Each cubic sample was loaded into a double-walled quartz glass tube and placed overnight in a furnace equipped with a resistance wire under vacuum. A solid cube sample was used to reduce blank effects. Each sample was heated stepwise to temperatures of 200, 450, 550, 700, 800, 900, and 1000 °C over 4 days (2 steps/day). After the sample was heated for 90 min at each step, the nitrogen and argon gases released from the samples were directed to a purification vacuum line designed to measure molecular nitrogen at the sub-nanomole level (Takahata et al., 1998). The procedure used for the purification of nitrogen gas is shown in Fig. 2. Carbon dioxide (CO_2) and water (H_2O) were trapped using liquid nitrogen (cold trap 1). Carbon monoxide, hydrocarbons, and hydrogen were then oxidised to CO_2 and H_2O using pure oxygen produced by a copper oxide finger heated to 850 °C and a platinum foil catalyst heated to 1000 °C. To resorb excess oxygen, the copper oxide furnace was cooled to 600 °C and finally to 450 °C. In this deoxidised state and in the presence of the platinum foil catalyst, nitrogen oxide gas was deoxidised to nitrogen gas (N_2). CO_2 and H_2O were adsorbed in cold trap 2 during the cooling of the copper oxide finger. A quadrupole mass spectrometer (QMS; HAL201, Hiden Analytical) was used to determine the sample size introduced to the mass spectrometer. The dilution process was repeated to obtain the proper sample volume. To detect the isotopes of trace nitrogen gas at the sub-nanomole level, we used the high-sensitivity static vacuum mass spectrometer (a modified VG3600, VG Micromass Ltd.) at the Atmosphere and Ocean Research Institute at the University of Tokyo. Nitrogen gas calibrated to nitrogen in air ($\delta^{15}N = 0\%$) was analysed before and after each sample. Repeated analysis of the standard over the course of 20 days showed that the overall reproducibility was 0.25% (Takahata et al., 1998). After the most recent sample

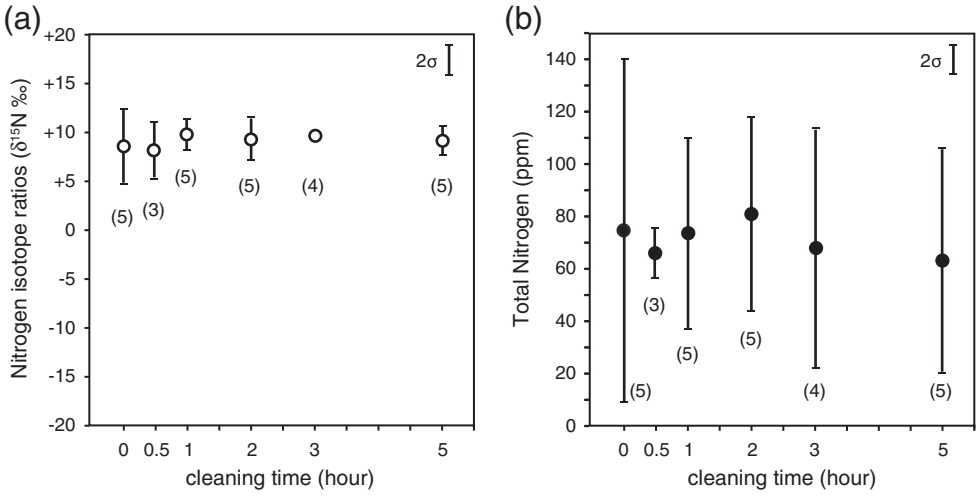

Fig. 1. The (a) $\delta^{15}N_{coral}$ and (b) total nitrogen content in a modern coral analysed by the chemical conversion methods reported by Yamazaki et al. (2011a). To analyse the nitrogen released by intra-crystalline organic matter, the modern coral powder was soaked in hot NaOH (60 °C, 2 N) before cleaning (for 0, 0.5, 1, 2, 3, and 5 h). The number in parentheses is the number of samples at each step. The error bar shows the uncertainty (2σ) at each cleaning time.

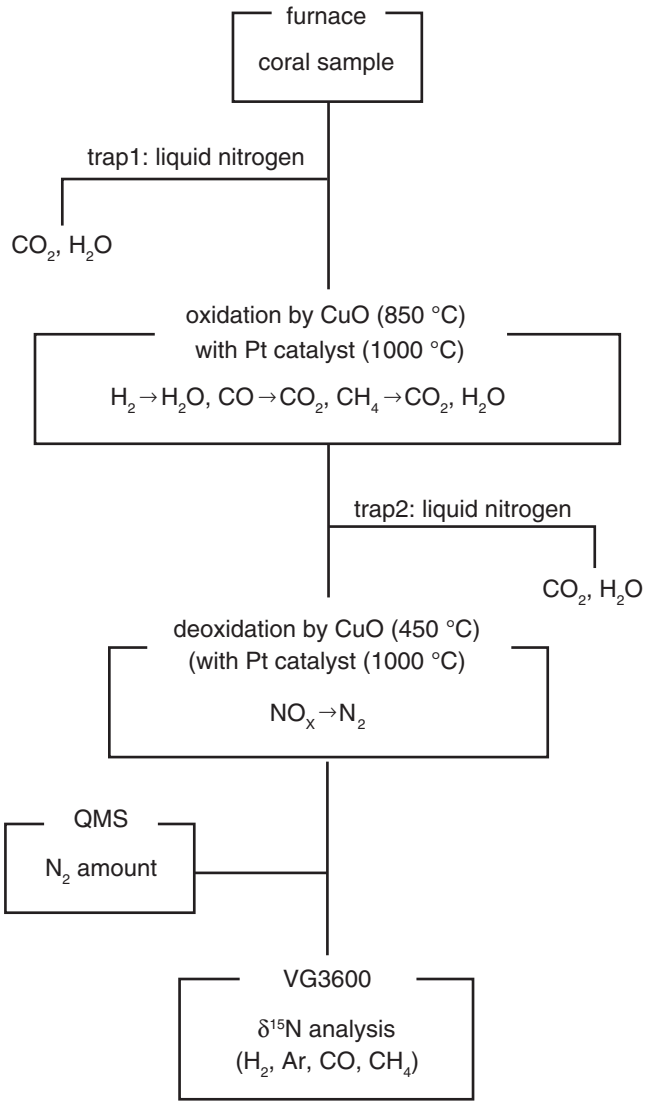

Fig. 2. Diagram of the nitrogen purification procedure used for nitrogen isotope analysis, which was performed using a modified noble gas mass spectrometer (VG3600).

was evaluated at 1000 °C, blank analyses were performed at 450 °C, and 1000 °C, to estimate the background noise.

3. Results and discussion

During the stepwise heating of the modern coral (Fig. 3a), the nitrogen concentration released from 200 °C, to 550 °C, was negligible (less than 1 ppm, where ppm is the parts per million of calcium carbonate). The nitrogen concentration was 41 ppm at 700 °C, 27 ppm at 800 °C, 26 ppm at 900 °C, and 5 ppm at 1000 °C. The total nitrogen concentration in the modern coral skeleton was 98 ppm. The $\delta^{15}N_{coral}$ ratios in the modern coral were +5.3% at 700 °C, +11.4% at 800 °C, +15.9% at 900 °C, and +11.4% at 1000 °C. The nitrogen/argon ratios (N_2/Ar) in the isotope analysis of the modern coral were 6980 at 700 °C, 6771 at 800 °C, 7563 at 900 °C, and 1385 at 1000 °C, indicating that the effects of air contamination (N_2/Ar: 83) were negligible. The bulk $\delta^{15}N_{coral}$ ratio in the modern coral, which was calculated using the expression shown below, was +10.1 ± 0.9 (2σ)%.

$$\delta^{15}N_{bulk} = \Sigma\left(fi \cdot \delta^{15}Ni\right)$$

where f is the fraction and i is the heating temperature step.

The modern bulk $\delta^{15}N_{coral}$ and total nitrogen content analysed by stepwise heating corresponded to the values measured by chemical conversion methods (+9.1 ± 1.5%, 63 ± 43 ppm).

The nitrogen released from the Pliocene coral skeleton (Fig. 3b) was less than 1 ppm at 200 °C. At the 450 °C. step, only a small amount of nitrogen was released (5 ppm). Subsequently, the concentration of nitrogen was 21 ppm at 550 °C, 14 ppm at 700 °C, 9 ppm at 800 °C, 7 ppm at 900 °C, and 18 ppm at 1000 °C. The $\delta^{15}N_{coral}$ ratios of the Pliocene coral were −0.5% at 450 °C, −0.7% at 550 °C, +2.9% at 700 °C, +14% at 800 °C, +6.9% at 900 °C, and +5.9% at 1000 °C. The nitrogen/argon ratios (N_2/Ar) in the isotope analysis of the Pliocene coral were 3389 at 550 °C, 4554 at 700 °C, 3407 at 800 °C, 7461 at 900 °C, and 4880 at 1000 °C, indicating that the effects of air contamination were negligible. The total nitrogen content in the Pliocene coral (69 ppm) was in agreement with the nitrogen content of modern corals (50–150 ppm: Marion et al., 2005; Yamazaki et al., 2011a,b; this study). The bulk $\delta^{15}N_{coral}$ ratio in the Pliocene coral was +4.4 ± 0.8 (2σ)%. The Pliocene $\delta^{15}N_{coral}$ was similar to the modern $\delta^{15}N_{nitrate}$ in the surface water of the tropical western

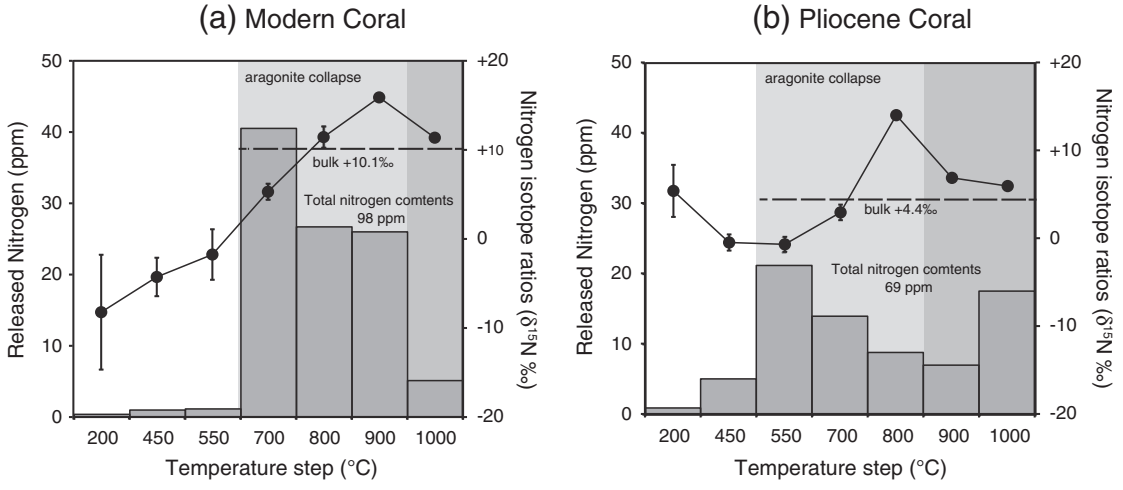

Fig. 3. Nitrogen isotopes (line, right axis) and released nitrogen gas (bar, left axis) at each heating step. The nitrogen isotope values (●) and corresponding uncertainty ($\sigma = \sqrt{(\sigma^2_{standard} + \sigma^2_{sample})}$) are plotted. (a) Living modern coral collected from Tatsukushi Bay, Kochi, Japan. (b) Pliocene fossil coral excavated from the Tartaro formation (3.5 Ma) located at Luzon Island, Philippines. Aragonite collapse temperatures (inside grey shading) were determined based on the maximum total nitrogen concentration. The dotted lines indicate the bulk nitrogen isotope values, which were calculated as $\delta^{15}N$ bulk = Σ(fi δ^{15}Ni) [f: fraction, i: heating temperature step].

Pacific (+3.6–+4.4%: Liu et al., 1996) and to the modern tropical $\delta^{15}N_{coral}$ (+2.5–+6.5%: Muscatine et al., 2005; Marion et al., 2005; Uchida et al., 2008; Yamazaki et al., 2011b). In the present study, the modern $\delta^{15}N_{coral}$ in Tatsukushi Bay was +5% higher than that of the Pliocene corals due to the latitudinal distribution of $\delta^{15}N_{nitrate}$. Yamazaki et al. (2011b) suggested that $\delta^{15}N_{coral}$ values in low latitudes (tropical to subtropical) decreased due to N_2 fixation ($\delta^{15}N$; −2-0%).

Cuif et al. (2004) reported that the thermal decomposition of coral aragonite begins to accelerate at 550 °C, which is supported by the fact that aragonite collapse triggered the maximum nitrogen release from the modern coral at 700 °C, and from the Pliocene coral at 550 °C,. The fossil coral was more brittle than the modern coral. After the collapse of aragonite, the $\delta^{15}N_{coral}$ values of the modern and Pliocene corals increased during the first three heating steps; however, at higher temperatures (900–1000 °C,), the $\delta^{15}N_{coral}$ values suddenly decreased and became similar to the bulk nitrogen isotope values. To examine kinetic fractionation effects during the release of nitrogen, a simple test can be performed. Namely, a plot of $\delta^{15}N_{coral}$ ratios remaining in the sample versus the amount of nitrogen remaining in the sample can be created using Rayleigh's law (Fig. 4, e.g., Boyd et al., 1993).

$$\ln R = \ln R_o + (1/\alpha - 1)\ln f,$$

where R is the isotopic ratio ($^{14}N/^{15}N$) of nitrogen remaining in the sample ($\ln [^{14}N/^{15}N]_{AIR} = 5.609$), R_o is the o`riginal isotopic composition of nitrogen in the sample, f is the fraction of nitrogen remaining in the sample, and α is the fractionation factor. The relationship between the $\delta^{15}N_{coral}$ values and the corresponding quantities of released nitrogen was linear. At higher temperatures, the $\delta^{15}N_{coral}$ results departed from the theoretical values expected for a Rayleigh distillation. At the three lower temperatures of aragonite collapse, the isotope fractionation factors (α) were 0.996 ($R^2 = 0.974$) for the modern coral and 0.995 ($R^2 = 0.996$) for the Pliocene coral. The internal skeletal structure collapsed during the high-temperature steps, which may have released fresh organic nitrogen, thus yielding lower nitrogen isotope ratios.

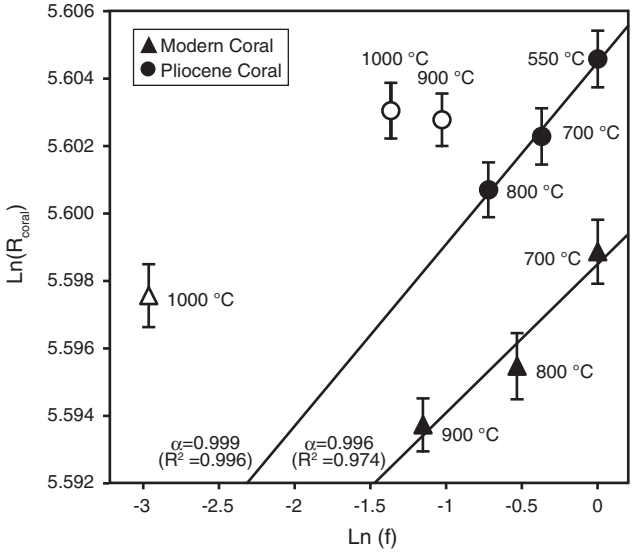

Fig. 4. Calibration lines for the kinetic fractionation of nitrogen isotopes during sample heating. R is the isotopic ratio ($^{14}N/^{15}N$) of nitrogen remaining in the sample ($\ln [^{14}N/^{15}N]_{AIR} = 5.609$), and f is the fraction of nitrogen remaining in the sample. The fractionation factors (α) were 0.996 ($R^2 = 0.974$) for the modern coral (▲) and 0.995 ($R^2 = 0.996$) for the Pliocene coral (●) and were calculated from values obtained in the lower three temperatures of aragonite collapse. The fractionation lines of nitrogen isotopes for the modern (△) and fossil (○) corals diverged at high temperatures.

The organic matrix in the coral skeletons may play a major role in the crystal nucleation process and in the micro- and macro-regulation of the crystal morphology in the biomineralisation process (reviewed by Cohen and McConnaughey, 2003; Allemand et al., 2004; Tambutte et al., 2011). Early in the calcification process, corals form centres of calcification (COCs). Subsequently, fibre-like aragonite surrounds the COCs (Pratz, 1882; Cuif and Dauphin, 1998). Geochemical analysis of the COCs indicated high concentrations of sulphur-bearing organic molecules (amino acids and sugars) and magnesium, which are more likely to fractionate in COCs than in fibres. Therefore, the organic matrix should be preserved in the inner skeletal structures that collapsed at higher temperature steps (900 °C–1000 °C). In the Pliocene coral, the nitrogen fraction at the 1000 °C step was greater than that at the (900 °C) previous step. This result suggests that nitrogen had been firmly preserved in the aragonite skeleton of the *Porites* coral since the Pliocene epoch.

Although more data are required, these results suggest that nitrogen in coral skeletons can withstand digenesis over long geological time scales. In future work, the time series of $\delta^{15}N_{coral}$ can be used as a proxy for nitrogen dynamics in palaeo-oceans. Our study showed that stepwise heating methods can effectively demonstrate the preservation of $\delta^{15}N_{coral}$ in modern and fossil corals.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2013.05.024.

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